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NEUTRAL AND CATIONIC COMPLEXES OF PALLADIUM(I) WITH ISOCYANIDES

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Summary

Palladium(I) complexes of formula $[PdX(RNC)_2]_n$ and $[Pd_2(RNC)_6]Y_2$ (X = Cl or Br, Y = Cl, Br, or PF_6, R = t-C_4H_9 or CH_3) have been synthesized and studied. Complexes of the first type were prepared by a novel coupling reaction between $[PdCl_2(PhCN)_2]$ and bis- (or tris)-(dibenzylideneacetone)palladium(0) in the presence of excess isocyanide. The complex $[Pd_2Cl_2(t\text{-}C_4H_9NC)_4]$ is identical to the product prepared by a different route by other workers. Reaction of $[Pd_2Cl_2(t\text{-}C_4H_9NC)_4]$ with $AgPF_6$ followed by addition of t-C_4H_9NC leads to $[Pd_2(t\text{-}C_4H_9NC)_6]$ $(PF_6)_2$. Addition of excess CH_3NC to $[PdX(CH_3NC)_2]_n$ leads to $[Pd_2(CH_3NC)_6]X_2$ (X = Cl or Br). The complex $[Pd_2(t\text{-}C_4H_9NC)_6](PF_6)_2$ is very stable, but complexes $[Pd_2(CH_3NC)_6]X_2$ are unstable in solid and solution towards loss of CH_3NC. It is concluded that the ionic complexes are structurally similar to $[Pd_2(CH_3NC)_6](PF_6)_2$, whose molecular structure is known to consist of two nearly planar "$Pd(CH_3NC)_3$" units joined by a Pd—Pd bond, and at ca. 90° to each other.

Introduction

The chemistry of palladium(I) has been little developed and is not well understood, in spite of the potential intermediacy of the univalent oxidation state in oxidation—reduction reactions or in oxidative aromatic coupling reactions [1,2]. At this time, only a few discrete compounds containing "univalent" palladium have been reported. These include the palladium(I) carbonyl halides $(R_4N)_2$-$[Pd_2X_4(CO)_2]$ (R = alkyl, X = Cl or Br) [3], the ligand bridged dimers I [4a], II [4b] and III [5], the benzene bridged IV [6], and its presumed analogue $[(C_6H_6Pd \cdot H_2O \cdot ClO_4]_n$ [1]. Also reported is a cyclohexadiene complex of

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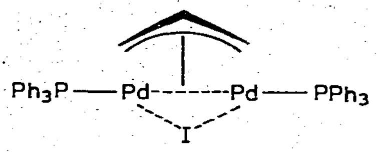
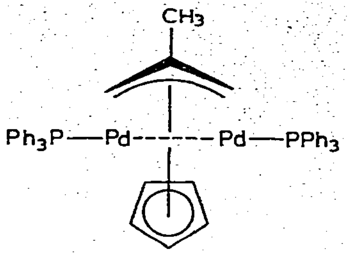


(I)



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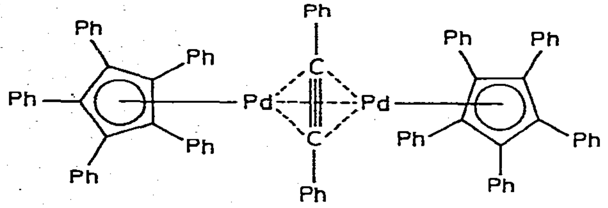

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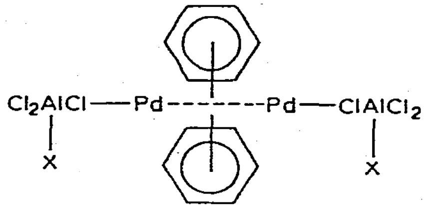


X = Cl or $AlCl_3$

(IV)

formula $[Pd_2(C_6H_8)(CH_3CO_2)_2 \cdot 0.5\,CH_3CO_2H]$ [7], a tetramer of formula $[(PPh_3)(PH_3)PdCl]_4$ [8], the dimeric isocyanide complexes of formula $[Pd_2X_2(t\text{-}C_4H_9NC)_4]$ (X = halide) and phosphine derivatives thereof [9], and finally $[Pd_2(CH_3NC)_6](PF_6)_2$ [10].

In the present communication we report a versatile new synthesis of some palladium(I) compounds of types $[Pd_2X_2(RNC)_4]$, $[Pd_2(t\text{-}C_4H_9NC)_6](PF_6)_2$, and $[Pd_2(CH_3NC)_6]X_2$ ($X = Cl^-$ or Br^-, $R = CH_3$ or $t\text{-}C_4H_9$). A convenient route to these compounds was developed in order to facilitate study of the palladium(I) oxidation state.

Results

Palladium(I) compounds were prepared according to eq. 1—4. $Pd(dba)_2$ and $Pd(dba)_3$ (dba = dibenzylideneacetone) were prepared by literature methods [11,12].

$$[PdCl_2(PhCN)_2] + [Pd(dba)_2] + 4\ t\text{-}C_4H_9NC \xrightarrow{PhCl} [Pd_2Cl_2(t\text{-}C_4H_9NC)_4] + 2\ dba + 2\ PhCN \qquad (1)$$

$$[PdX_2(PhCN)_2] + [Pd(dba)_3] + 2\ CH_3NC \xrightarrow{PhCl} [PdX(CH_3NC)_2]_n + 3\ dba + 2\ PhCN \qquad (2)$$

$$[Pd_2Cl_2(t\text{-}C_4H_9NC)_4] + 2\ AgPF_6 + 2\ t\text{-}C_4H_9NC \xrightarrow{acetone} [Pd_2(t\text{-}C_4H_9NC)_6](PF_6)_2 + 2\ AgCl \qquad (3)$$

$$[PdX(CH_3NC)_2]_n + \text{excess } CH_3NC \xrightarrow{\text{acetone}} [Pd_2(CH_3NC)_6]X_2 \ (X = Cl^- \text{ or } Br^-) \quad (4)$$

The complex $[Pd_2Cl_2(t\text{-}C_4H_9NC)_4]$ is dimeric in chloroform and in benzene [9] solutions, and is a non-conductor in nitromethane solution. The $t\text{-}C_4H_9NC$ groups appear as a singlet in ^1H NMR, both at room temperature and at −60°C in $CDCl_3$. It was observed that exchange of coordinated and free $t\text{-}C_4H_9NC$ is rapid at room temperature and slow at −60°C, but a detailed study of the exchange was not undertaken. Reaction of $[Pd_2Cl_2(t\text{-}C_4H_9NC)_4]$ with CH_3NC in chloroform is instantaneous. In this reaction, a slightly soluble yellow product having nearly all of the $t\text{-}C_4H_9NC$ replaced by CH_3NC was obtained, but the product was not fully characterized.

The complexes $[Pd_2(CH_3NC)_6]X_2$ are unstable as solids and in solution towards loss of CH_3NC. The solid materials change from off-white to pale yellow in a few hours at room temperature, and there is a strong odor of CH_3NC above the material. In solution in CH_2Cl_2 weak absorption for free CH_3NC is observed along with the coordinated $\nu(NC)$ at $\sim 2230 \text{ cm}^{-1}$.

The infrared and ^1H NMR data obtained for the various compounds are presented in Table 1.

In order to correctly ascertain the molecular formula of $[Pd_2(t\text{-}C_4H_9NC)_6](PF_6)_2$, its equivalent conductance (Λ) (as well as the equivalent conductances of a number of standard electrolytes) was determined as a function of concen-

TABLE 1

INFRARED AND NUCLEAR MAGNETIC RESONANCE RESULTS

Compound	NMR (δ, ppm)	$\tilde{\nu}(NC)$ (cm^{-1})	Far infrared spectrum (cm^{-1}) (Nujol)
$t\text{-}C_4H_9NC$		2135 (PhCl or CH_2Cl_2)	
$[Pd_2Cl_2(t\text{-}C_4H_9NC)_4]$	1.53s ($CDCl_3$)	2173(br) (KBr)	520s (sh); 508s; 440m; 398m; 370w; 342w; 294m; 258vs; 240m (sh); 200w
$[Pd_2(t\text{-}C_4H_9NC)_6](PF_6)_2$	1.67s (CD_3COCD_3) 1.70s ($PhNO_2$) 1.60s ($CDCl_3$)	2235w (sh); 2220m (sh); 2202s ($CHCl_3$)	558s; 522m; 452w; 400m; 340w; 298w; 236w
CH_3NC	3.14 (t, J 2 Hz) ($CDCl_3$)	2167 (CH_2Cl_2)	
$[PdCl(CH_3NC)_2]_n$	3.41s ($CDCl_3$)	2220 (CH_2Cl_2) 2222 (Nujol)	454s; 316m; 250s; 205w
$[PdBr(CH_3NC)_2]_n$		2215(br) (Nujol) 2217 (CH_2Cl_2)	480w; 435s; 318m; 283w; 210m; 168w
$[Pd_2(CH_3NC)_6]Cl_2$	3.51s ($CDCl_3$)	2227s, 2250(sh) (CH_2Cl_2) 2220—2260(br) (HCBD)[a]	458vw; 431s; 420m (sh); 372w; 323w; 222w
$[Pd_2(CH_3NC)_6]Br_2$		2235(br) (HCBD) 2255w (sh); 2250m (sh); 2235s (sh); 2230s (Nujol)	446vw; 428s; 418m (sh); 372w; 351w; 322w; 220w

[a] HCBD = hexachlorobutadiene.

TABLE 2

CONDUCTANCE OF ELECTROLYTES IN NITROBENZENE AT 25°C (This work)

Compound	Concentration range (Normality)	Λ_0[a] (Ω^{-1} cm^{-1} N^{-1})	λ[b] (Ω^{-1} cm^{-1} $N^{-3/2}$)
$[(n\text{-}C_4H_9)_4N]Br$	8.70×10^{-3}—4.03×10^{-5}	30.9	101
$[(n\text{-}C_4H_9)_4N]I$	8.79×10^{-3}—3.43×10^{-5}	37.0	110
$\{Rh[C_5(CH_3)_5][C_6H_3(CH_3)_3]\}(PF_6)_2$	7.84×10^{-3}—1.21×10^{-5}	36.2	190
$[Pd_2(t\text{-}C_4H_9NC)_6](PF_6)_2$	8.08×10^{-3}—3.75×10^{-5}	36.8	155
$[Pd_2(t\text{-}C_4H_9NC)_6](PF_6)_2$	3.97×10^{-3}—9.17×10^{-6}	41.0	172

[a] Λ intercept at zero concentration for plot of Λ_N vs. $N^{1/2}$ (N is equivalent concentration). [b] Slope of Λ_N vs. $N^{1/2}$.

TABLE 3

CONDUCTANCE OF ELECTROLYTES IN NITROBENZENE AT 25°C (Literature sources)

Compound	Concentration range (Normality)	Λ_0[c] (Ω^{-1} cm^{-1} N^{-1})	λ[d] (Ω^{-1} cm^{-1} $N^{-3/2}$)	Ref.
$[(n\text{-}C_4H_9)_4N]Br$	5×10^{-3}—5×10^{-5}	33.7	117	13a
$[(n\text{-}C_4H_9)_4N]BF_4$	1.5×10^{-3}—6×10^{-5}	34.1	89	13a
$[Au(dtc)_2]^+[AuBr_2]^-$ [a]	5×10^{-3}—4×10^{-5}	30.7	70	13b
$[Au(bipy)(C_2H_5)_2]^+[AuBr_2(C_2H_5)_2]^-$ [b]	3×10^{-3}—2×10^{-4}	28	60	13c
$[Rh(bipy)_2Cl_2]ClO_4$	9×10^{-4}—2×10^{-5}	32	185	13d
$[Co(bipy)_3](ClO_4)_2$	9×10^{-4}—2×10^{-5}	37	201	13d
$[(C_6H_5)_4As]_2[Co(NCS)_4]$	2×10^{-3}—4×10^{-4}	29.4	130	13e
$[(C_6H_5)_4As]_2[Co(NCSe)_4]$	2×10^{-3}—4×10^{-4}	30.2	156	13e
$[Rh(bipy)_3](ClO_4)_3$	9×10^{-4}—2×10^{-5}	41	334	13d

[a] dtc = *N,N*-di-n-butyldithiocarbamate. [b] bipy = 2,2-bipyridyl. [c] See footnote *a* of Table 2. [d] See footnote *b* of Table 2.

tration. The results are presented in Table 2. Some relevant conductance results taken from literature sources are found in Table 3. The compound is diamagnetic in solution.

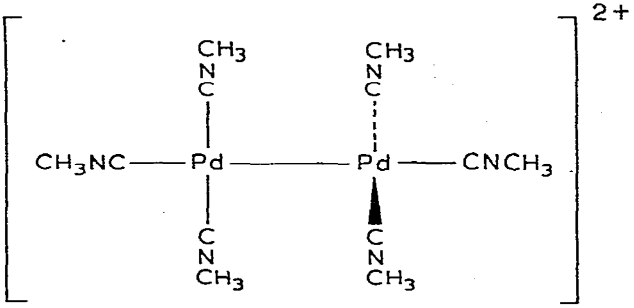
Discussion

The dimeric complex $[Pd_2Cl_2(t\text{-}C_4H_9NC)_4] \cdot C_6H_5Cl$ has been reported previously by Otsuka et al. [9]. We obtained the complex (chlorobenzene free) by Otsuka's method followed by crystallization from toluene, and we find that the chlorobenzene-free Otsuka complex has spectral characteristics identical to those of $[Pd_2Cl_2(t\text{-}C_4H_9NC)_4]$ prepared by the more convenient method reported here. Our method makes use of a novel coupling reaction between starting materials which are easily prepared in high yields: $[Pd(dba)_2]$ [11] and $[PdCl_2(PhCN)_2]$ [14]. No isolation of intermediate isocyanide products is necessary, and the desired palladium(I) complex crystallizes directly from the reaction mixture on cooling. The reaction is also versatile, as other halides and isocyanides may be employed.

Otsuka and co-workers concluded from IR data that the diamagnetic complexes $[Pd_2X_2(t\text{-}C_4H_9NC)_4]$ (X = Cl, Br, I) have only terminal isocyanides

(ν(NC) $\cong 2170$ cm^{-1}) and bridging halogens (ν(Pd—Cl) $= 259$ cm^{-1}). Our IR data for the chloride dimer agrees with the earlier report. On the basis of known far IR results with Pd(II)—Cl complexes, the low Pd—Cl stretching frequency observed for [$Pd_2Cl_2(t\text{-}C_4H_9NC)_4$] would suggest bridging chlorine. Goggin and Mink [3a], however, have reported an extensive synthetic and vibrational study of palladium(I) carbonyl halide complexes. They conclude from the vibrational study that dimeric anions of the type [$Pd_2X_4(CO)_2$]$^{2-}$ have all-terminal halogens and both carbonyl groups bridging. The IR active Pd—Cl stretching vibrations in [$Pd_2X_4(CO)_2$]$^{2-}$ were assigned to bands at 271 and 260 cm^{-1}. In addition the X-ray characterized [3b] anion [$Pt_2Cl_4(CO)_2$]$^{2-}$ has all terminal chlorines with ν(Pt—Cl) $= 270$ and 240 cm^{-1} [3c]. These M(I)—Cl structural studies leave open the possibility that the halogens are terminal in [$Pd_2X_2(t\text{-}C_4H_9NC)_4$].

The ionic complex [$Pd_2(t\text{-}C_4H_9NC)_6$] ($PF_6$)$_2$ was prepared from [$Pd_2Cl_2(t\text{-}C_4H_9NC)_4$] as outlined in eq. 3. A probable methyl isocyanide analogue to [$Pd_2(t\text{-}C_4H_9NC)_6$] ($PF_6$)$_2$ has been prepared by a completely different route [10]. The molecular structure of the methyl isocyanide complex was determined [10] and the structure of the cation is shown schematically in V.



(V)

The halves of the dimeric cation are joined solely by the Pd—Pd bond (2.531 Å), and the two nearly square-planar palladium environments lie at a dihedral angle of 86.2°. The infrared spectrum of [$Pd_2(CH_3NC)_6$] (PF_6)$_2$ shows only terminal N≡C bands at 2260, 2252, 2240, and 2234 cm^{-1} [10]. The frequency shifts on coordination and the pattern of frequencies observed for coordinated RN≡C are remarkably similar in [$Pd_2(CH_3NC)_6$] (PF_6)$_2$ [10] and [$Pd_2(t\text{-}C_4H_9NC)_6$] ($PF_6$)$_2$. Thus the IR, conductance, and magnetic results for the latter compound lead us to the conclusion that its structure is similar to that shown in V.

The methyl isocyanide complexes [$PdX(CH_3NC)_2$]$_n$ were prepared as outlined in eq. 2. Unfortunately, molecular weights for these complexes could not be obtained because of instability in solution. The IR spectra again show only terminal N≡C stretching. The absorption at 250 cm^{-1} in [$PdCl(CH_3NC)_2$]$_n$ is assigned to $\bar{\nu}$(Pd—Cl) (by comparison, $\bar{\nu}$(Pd—Cl) is at 258 cm^{-1} for [$Pd_2Cl_2(t\text{-}C_4H_9NC)_4$] and there is no strong absorption in the region 150—435 cm^{-1} in [$PdBr(CH_3NC)$]$_n$). The spectral and analytical results for [$PdX(CH_3NC)_2$]$_n$ suggest that these complexes are structurally similar to [$Pd_2Cl_2(t\text{-}C_4H_9NC)_4$].

The complex $[Pd_2Cl_2(t\text{-}C_4H_9NC)_4]$ shows no tendency to add additional $t\text{-}C_4H_9NC$. In contrast, the complexes $[PdX(CH_3NC)_2]_n$ readily react with CH_3NC to produce $[Pd_2(CH_3NC)_6]X_2$, X = Cl or Br. The near and far infrared spectra of $[Pd_2(CH_3NC)_6]X_2$ are identical, which places the halogen outside the coordination sphere. In addition, only terminal N≡C stretching modes are observed. Finally, the published near IR results [10] for $[Pd_2(CH_3NC)_6](PF_6)_2$ are nearly identical to our results for $[Pd_2(CH_3NC)_6]X_2$, and the far IR spectrum of $[Pd_2(CH_3NC)_6](PF_6)_2$, prepared according to the literature procedure [10], is virtually identical to the far IR's of $[Pd_2(CH_3NC)_6]X_2$. These observations strongly suggest that the complexes $[Pd_2(CH_3NC)_6]X_2$ (X = Cl, Br) are structurally analogous to $[Pd(CH_3NC)_6](PF_6)_2$.

The relative instability of $[Pd_2(CH_3NC)_6]X_2$ towards loss of CH_3NC is doubtless related to the nucleophilicity of halide and the volatility of CH_3NC. The inability of $[Pd_2Cl_2(t\text{-}C_4H_9NC)_4]$ to add additional $t\text{-}C_4H_9NC$ (with chloride displacement) can be ascribed to steric interference of the bulky t-butyl groups. The complex $[Pd_2Cl_2(t\text{-}C_4H_9NC)_4]$ does however interact with $t\text{-}C_4H_9NC$ as shown by the fast exchange of free and coordinated $t\text{-}C_4H_9NC$.

The reaction of palladium(II) and palladium(0) complexes to give complexes containing palladium(I) with suitable ligands is clearly a reaction of substantial potential which is being further explored.

Experimental

Reagent grade acetone was dried by distillation from $MgSO_4$. Reagent grade chlorobenzene was doubly distilled at atmospheric pressure. Tris(dibenzylideneacetone)palladium(0) [12], bis(dibenzylideneacetone)palladium(0) [11], dibromobis(benzonitrile)palladium(II) [14], dichlorobis(benzonitrile)palladium(II) [14], and the ligand isocyanides [16] were prepared by literature methods.

For the conductance measurements two bridges were used: (a) Industrial Instruments Model R16B, operating at 1000 Hz Ac, and (b) US Army Surplus AN/URM-90, operating at 1000 Hz AC (for measurement of resistances up to $1.1 \times 10^7\ \Omega$).

An unplatinized conductivity cell was used. The cell had two approximately 1 cm^2 Pt electrodes separated by approximately 1 cm. The cell was calibrated with 0.00100 *M* KCl in distilled, nitrogen saturated water (0.00100 *M* KCl has $L = 1.469 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ at 25°C). The cell constant k was found to be 0.319 cm^{-1} at either 60 or 1000 Hz, which indicates that polarization effects were not important for aqueous 0.00100 *M* KCl. Measurements on nitrobenzene solutions of the dilute electrolytes were also not significantly dependent upon frequency. The temperature was regulated to 25 ± 0.05°C for all measurements. For conductance measurements, 250 ml Baker "Analyzed" nitrobenzene was passed slowly through a 2.5 × 25 cm column of Matheson, Coleman, Bell activated Al_2O_3, 80—325 mesh. Polynitrobenzenes were separated as a bright yellow band. The specific conductivity of nitrobenzene prepared in this way was less than or equal to $3 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$ (this upper limit is imposed by the bridge, the measured resistance was $\geqslant 1.1 \times 10^7\ \Omega$).

NMR spectra were determined using a Perkin—Elmer R12B instrument. Infrared spectra were determined on Perkin—Elmer 157, 180, and 621 instruments. Molecular weights were determined using a Mechrolab vapor pressure osmometer.

Dichlorotetrakis(t-butylisocyanide)dipalladium(I), [$Pd_2Cl_2(t\text{-}C_4H_9NC)_4$]

90 ml redistilled chlorobenzene was placed in a side-arm vessel (filter flask or Schlenk tube) and argon was bubbled through the chlorobenzene for 15 minutes. The argon was then introduced through the sidearm, and 5.40 g [Pd(dba)$_2$] (9.4 mmol) was added, followed by 4.85 ml t-C_4H_9NC (3.7 g, 44.5 mmol). The mixture was stirred until practically all of the dark solid dissolved to give a straw-colored solution * (ca. 15 min), and 3.60 g solid [$PdCl_2(PhCN)_2$] (9.4 mmol) was added in fractions over a few minutes **. The yellow-brown solution was stirred under argon for 45 minutes, during which time crystallisation commenced and the color of the solution darkened. The reaction mixture was closed under argon and was placed in the freezer overnight (ca. —35°C). The yellow to yellow-green precipitate was filtered and washed with 50 ml portions of anhydrous ether until the washes were colorless (some dibenzylideneacetone may precipitate, and about three 50 ml washes with ether remove this impurity). The yellow to yellow-green solid was air-dried. The crude yield is 5.65 g (98%).

For purification, the crude product was dissolved in dichloromethane (8 ml/g) and was gravity filtered through a fine mesh paper (Whatman No. 542 or equivalent). The product was precipitated by dropwise addition of anhydrous diethyl ether to the dichloromethane solution, until 5 ml ether had been added for every one ml of dichloromethane solution originally present. The mixture was chilled for several hours at —35°C, filtered, washed with ether, and air-dried.

Traces of dichloromethane are removed by vacuum drying for 2 h at 56°C/ 0.01 mmHg. The yield is 5.03 g (87% based on [Pd(dba)$_2$]). Anal. Found: C, 39.31, 38.77; H, 6.10, 6.13; Cl, 11.67, 11.50; N, 9.05, 9.33; Pd, 34.8; mol. wt. 614. $C_{20}H_{36}N_4Cl_2Pd_2$ calcd.: C, 38.98; H, 5.89; Cl, 11.55; N, 9.09; Pd, 34.55%; mol. wt. 616.2. The compound is a non-conductor in nitromethane.

Hexakis(t-butylisocyanide)dipalladium(I)dihexafluorophosphate, [$Pd_2(t\text{-}C_4H_9NC)_6]_2(PF_6)_2$

500 mg (0.81 mmol) [$Pd_2Cl_2(t\text{-}C_4H_9NC)_4$] was dissolved in 10 ml dry acetone at —20°C, under an atmosphere of argon. To this solution was added 410 mg (1.62 mmol) $AgPF_6$, followed by stirring at —20 to —25°C for 10 minutes. The resulting greenish mixture was filtered by gravity through Whatman No. 542 paper (an atmosphere of nitrogen was maintained above the funnel). The brown filtrate was passed directly into 2 ml acetone containing 200 μl (1.88 mmol) t-C_4H_9NC. The precipitate was washed with two 5 ml portions of acetone, both of which were collected with the original filtrate. The combined filtrates were reduced in volume on the rotary evaporator to about 8 ml, and 25 ml anhydrous ether was added. The gray powder produced was filtered off and was air dried. The yield was 534 mg (66%, crude).

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* Traces of Pd metal present in the [Pd(dba)$_2$] can cause the solution to appear greenish, and leave a small amount of dark, insoluble deposit.

** Approximately 5 fractions. This is not a critical variable. Traces of Pd metal can cause the precipitate to appear greenish (Pd is removed on recrystallisation).

For purification, the entire crude product was dissolved in 5 ml dry acetone and the solution was filtered through Whatman No. 542 paper, which resulted in a black residue and a yellow filtrate. Ether was added to the filtrate until precipitation commenced and the mixtue was allowed to stand at ambient temperature for 30 minutes. The mixture was filtered, washed with ether, and air dried, resulting in 320 mg of an off-white powder. This was similarly recrystallized a second time to yield 280 mg off-white needles (35%, based on starting Pd), which decomposed at 140 to 150°C to a brown substance. The material was vacuum dried over boiling acetone for 1 h at ≈ 0.1 mmHg. Anal. Found: C, 35.69; H, 5.48; N, 8.39. $C_{30}H_{54}N_6F_{12}P_2Pd_2$ calcd.: C, 35.93; H, 5.43; N, 8.38%.

The ^1H NMR spectrum of the product in $(CD_3)_2CO$ showed a sharp singlet at δ 1.67 ppm. Silver was undetectable in the emission spectrogram of a sample of this product. A trace (est. ~2%) of $AgNO_3$ was added to a second sample of the product, and emission lines for silver were clearly discernable. The ^1H NMR spectrum of $[Pd_2(t\text{-}C_4H_9NC)_6](PF_6)_2$ in nitrobenzene consists of a sharp singlet at δ 1.70 ppm which is unchanged after 1 h. The infrared spectrum of the NMR solution after 1 h and 15 min shows a single absorption at 2200 cm^{-1}. Both the NMR and IR results agree with results in $CDCl_3$ or with mulls or pellets (IR). The complex was found to be diamagnetic in chloroform solution by means of the Evans susceptibility method [17].

$[PdCl(CH_3NC)_2]_n$

10 ml chlorobenzene was deoxygenated in the Schlenk tube by bubbling argon for 15 minutes. To the chlorobenzene was added 0.809 g (1.0 mmol) $[Pd(dba)_3]$ and 330 μl (6.0 mmol) CH_3NC. After 15 minutes the solution was orange and there was a considerable amount of dark oil present. The supernatant orange solution was decanted into a second Schlenk tube, and the dark oil was discarded. 0.383 g (1.0 mmol) $[PdCl_2(PhCN)_2]$ was added to the orange solution and in a few minutes an orange-tan precipitate appeared. After 3 h stirring at room temperature, an additional 100 μl CH_3NC added, but no change was observed. After two additional hours stirring, the solid was filtered under a nitrogen atmosphere, was washed with ether, and was dried by passing nitrogen through the funnel. The medium yellow crude product weighed 400 mg.

350 mg of the crude product was slurried with 200 ml warm CH_2Cl_2, followed by filtration through Whatman No. 1 paper under a nitrogen blanket. The volume of solvent was then reduced to a ca. 10 ml on a rotary evaporator, at which time a yellow precipitate appeared. After 2 h standing, the mixture was filtered under nitrogen, was washed with ether, and was dried in a nitrogen stream. The bright yellow powder was evacuated (0.005 mmHg) for 30 min over refluxing CH_2Cl_2. The yield was 150 mg. Anal. Found: C, 21.65, 21.60; H, 2.91, 2.97; Cl, 15.69; N, 12.86, 12.63. $C_8H_{12}N_4Cl_2Pd_2$ calcd.: C, 21.45; H, 2.70; Cl, 15.83; N, 12.51%.

This preparation was also carried out using $[Pd(dba)_2]$ and a reaction time of 2 h. Found: C, 21.84; H, 3.04; Cl, 15.98; N, 12.28.

Hexakis(methylisocyanide)dipalladium dichloride, $[Pd_2(CH_3NC)_6]Cl_2$

30 mg $[PdCl(CH_3NC)_2]_n$, 4 ml dry acetone, and 100 μl CH_3NC were stirred

under N_2 at room temperature for 50 h. (The reaction mixture did not visibly change after 1 h.) The nearly white precipitate was filtered under nitrogen and was dried by the nitrogen stream. The product was analyzed for C, H, Cl, N, within minutes of its isolation: Anal. Found: C, 26.57; H, 3.77; Cl, 13.14; N, 16.15%. $C_{12}H_{18}N_6Cl_2Pd_2$ calcd.: C, 27.19; H, 3.42; Cl, 13.38; N, 15.86.

$[PdBr(CH_3NC)_2]_n$

The synthesis was similar to that described for $[PdCl(CH_3NC)_2]_n$. Thus 809 mg $[Pd(dba)_3]$, 470 mg $[PdBr_2(PhCN)_2]$, and 330 μl CH_3NC were stirred for 2 h in chlorobenzene, followed by filtration under nitrogen. All attempts to recrystallize the 425 mg bright yellow product failed, due to insolubility at reasonable temperatures and dissociation of higher temperatures. The crude product was evacuated (0.005 mmHg) over refluxing CH_2Cl_2 for 30 min and elemental analysis was not attempted. The material decomposed at 215—220°C to a dark oil.

Hexakis(methylisocyanide)dipalladium(I) dibromide, $[Pd_2(CH_3NC)_6]Br_2$

75 mg of crude $[PdBr(CH_3NC)_2]_n$ and 150 μl CH_3NC were stirred for 4 h in dry acetone, followed by filtration to yield an off white powder. Near and far infrared spectra of this material were determined immediately, as the compound reverted to yellow on standing at room temperature for ca $\frac{1}{2}$ h.

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